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Preparation of Silica Gel from Rice Husk Ash Using Microwave Heating

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Abstract

The purpose of this research is to separate silica gel from rice husk ash by microwave heating. The experiments were performed by heating rice husk ash in sodium hydroxide solution with various concentrations in microwave oven for 5 or 10 minutes. The obtained sodium silicate was neutralized to give silica gel. The best condition for silica gel production was the reaction with 2.0 M sodium hydroxide at microwave power of 800 W for 10 minutes. The ability of silica gel as desiccant was investigated by adsorption test. The results showed that silica gel prepared by low concentration of sodium hydroxide solution had the highest ability of water adsorption. The power of microwave and volume of reactions seemed to have only little effect.

Key words: Rice husk ash, Silica gel, Waste utilization, Microwave, Dielectric heating, Sodium silicate

Introduction

Burning rice husk as fuel to generate energy resulted in a waste product, namely rice husk ash. Rice husk ash is rich in silica (92-97%) and can be an economically viable raw material for production of silica gel and powders. Silica gel is the amorphous (noncrystalline) form of SiO_2. It has a large surface area (~500 m^2/g), which allows silica gel for showing great water adsorption ability via chemisorptions on Si-OH groups. Silica gel from rice husk ash can be roughly prepared by 2 ways, that is to say the thermal treatment with temperatures ranging from 500-1400°C. This method requires high temperature.[1, 2] The second way of preparation is leaching by acid or basic solutions Kalapathy, *et al*. (2000) and (2002) and then neutralization by acid to produce silica gel. The latter consumes low energy, and is cost-effective compared to the current melting method. Besides this advantage, the process may decrease CO_2 emission due to the current manufacture of sodium silicate from the reaction of Na_2CO_3 and SiO_2. Reaction efficiency of the reaction between NaOH and SiO_2 is estimated by 2 ways. One way is by ratio of the weight of silica gel obtained from the reaction and the weight of silica content in rice husk ash. Another way is to calculate the SiO_2/Na_2O ratio of the system. The reaction between NaOH and SiO_2 of rice husk ash can be expressed as the following reaction.

$$2xNaOH + ySiO_2 \rightarrow xNa_2O{\cdot}ySiO_2 + xH_2O \qquad (1)$$

And silica gel can be produced by neutralization of the obtained sodium silicate ($xNa_2O{\cdot}ySiO_2$) as follows.

$$xNa_2O{\cdot}ySiO_2 + xH_2SO_4 \rightarrow ySiO_2 + xNa_2SO_4 + xH_2O \qquad (2)$$

If the mol of NaOH used in reaction (1) is lower than the mol of SiO_2 of rice husk ash, NaOH becomes the limiting reagent of the reaction. Thus the ratio of SiO_2 and Na_2O (y/x) can be calculated by use of mol of $ySiO_2$ (silica gel obtained) and mol of 2xNaOH (NaOH used in the reaction).

One problem of the leaching process by NaOH is the corrosion of reactors which is caused from use of the strong base. The problem can be solved by making use of microwave (MW) heating because microwave can heat up substances even in plastic containers, which are not damaged by NaOH solution.

Recently, use of MW heating leads to many interesting results in chemical reactions. The conventional heating by heater and oil bath is known as convection heating. But MW heating is a so-called, dielectric heating, which directly interacts with the molecules and usually gives higher reaction efficiency with traces amount of by-products. It was found, for example, that phosphorylation of cellulose from rice straw could be completed in 1-2 minutes by microwave while it required at least 2 hours for conventional heating.[6]

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In this work, the use of MW heating for preparation of silica gel from rice husk ash is proposed. The effect of the reaction time, NaOH concentration, and microwave power on the yields of silica gel was investigated. Furthermore, water adsorption ability of the obtained silica gel was examined in comparison with the silica gel prepared from conventional method.

Materials and Experimental Procedures

Material and Apparatus

Rice husk ash was collected from a local rice mill factory. It was dried at 150°C for 24 hours to remove water content. The obtained RHA was used in the experiment without any pre-treatment. Sodium hydroxide (99%), sulfuric acid (98%), HCl (38%), Na_2CO_3 and NH_3 solution were acquired from Ajax fine chem. All chemicals were reagent grade or analytical grade and used as received. The microwave oven was Electrolux EMM 2005, which can adjust its power within the range of 300-800 W. The conventional heater was from Grant instrument (W28) with a power of 1500 W.

Preparation of Silica Gel

10 g of rice husk ash were added to various volumes and concentrations of sodium hydroxide solution (most solutions were 2.0 M = 165 ml, 1.0 M = 330 ml, 0.5 M = 660 ml, because the above solutions provide a minimum amount of NaOH to produce sodium silicate with SiO_2/Na_2O ratio = 1.0) in a thermo-resistant plastic container. The mixture was then heated by microwave irradiation at 400 W, 600 W or 800 W at 100°C for 5 min or 10 min. The solution was filtered through filter paper (10 μm) and the carbon residue was washed with 100 ml of de-ionized water. The filtrate and washing were allowed to cool to room temperature. Concentrated sulfuric acid was added to the obtained solution until pH 7.0 and incubated for 48 hours to promote silica gel formation. The silica gel produced was separated from soluble salt solution by vacuum filtration and washed with de-ionized water. Then silica gel was dried at 150°C for 48 hours and ground into powder. The obtained silica gel was white rough powder. The samples for XRD analysis were heated with 200 ml of 2 M hydrochloric acid solution by MW heating for 10 min, then rinsed with de-ionized water dried at 150°C for 24 hours Some experiments were performed in a glass beaker (500 ml) using conventional heating in oil bath (1500 W) in order to compare the effect of heating methods. The reaction conditions were the same as microwave heating as listed in Table 1, except for the heating method.

The reaction temperature could not be kept constant during the reaction because the reactions started at room temperature. However, the temperature of all reactions became constant at 100°C after they reached the boiling point of water.

Measurement of Water Adsorption Ability

The silica gels before treatment of hydrochloric acid were used in this experiment. 3 g of dried silica gel in a small container was placed in desiccators, the atmosphere of which was saturated with moisture by placing 100 ml of water in a beaker inside. The change of weight of silica gel was recorded everyday for a period of 10 days.

Results and Discussion

Comparison Between Conventional Heating and MW Heating, and Effect of Concentration

Table 1 shows the weights of silica gels obtained from MW heating and conventional heating in oil bath at various reaction times and concentrations. Moles of sodium hydroxide of all conditions were fixed at 0.33 moles in order to provide enough sodium content for the reactions. The reaction times of microwave were fixed at 5 or 10 min because the reaction systems run out of water at 30 min.

It was found that for every sodium hydroxide concentration, MW heating at 800 W yielded more silica gel than conventional heating. Especially MW heating at 600 W (1.0 M NaOH) gave almost 1.6 times the amount of conventional heating. For 0.5 M of NaOH, the effect of using microwave at low power showed a quite low yield of product. The energy supplied from MW might not provide enough heat for a large volume of solution (660 ml) to keep a long boiling point in 5 or 10 min.

On the other hand, 2.0 M of NaOH, which is a strong basic solution, showed great ability for leaching silica gel from rice husk ash. Hence the effect from the use of MW was not obvious as in the case of 1.0 M NaOH. Table 1 also compared the results with the yields from sea sand as silica source. It was found that most conditions could not generate any silica gel. Conventional heating for 1 hour gave only 0.3% of silica gel. The result confirms that leaching of silica by NaOH is suitable for reaction of rice hush ash because of its amorphous nature. The amorphous morphology of silica gels from all reactions was confirmed by XRD measurement of silica gels after treatment with HCl.

Table 1. Weight (g) of silica gel obtained as the effect of heating methods and MW power

$NaOH_{aq}$ concentration and volume	Time (min)	Microwave 400 W	Microwave 600 W	Microwave 800 W	Oil bath	Oil bath vs sea sand
0.5 M, 660 ml	5	0.000*	0.000	1.632	1.308	0.000*
	10	0.000*	2.060	3.611	3.255	0.000*
	30	-**	-**	-**	5.365	0.000*
	60	-**	-**	-**	8.173	0.000*
1.0 M, 330 ml	5	0.886	2.961	3.407	1.885	0.000*
	10	3.440	6.340	6.830	3.997	0.000*
	30	-**	-**	-**	6.465	0.093
	60	-**	-**	-**	8.900	0.245
2.0 M, 165 ml	5	1.940	4.994	7.313	5.516	0.000*
	10	4.000	8.959	9.595	6.873	0.000*
	30	-**	-**	-**	9.060	0.221
	60	-**	-**	-**	10.143	0.299

Note: * Silica gel could not be obtained. ** MW heating was not performed at 30 and 60 min.

Generally Na_2CO_3 is used for reaction with quartz sand at temperatures > 1100°C to generate silicate salts. We also compared reaction of RHA with various kinds of bases to find the possible uses of other chemicals. The results are listed in Table 2.

Table 2. Weight (g) of silica gel resulting from base chemicals when heated by MW at 800 W

Chemicals	0.5 N		1.0 N		2.0 N	
	5 min	10 min	5 min	10 min	5 min	10 min
NaOH	1.632	3.611	3.408	6.830	7.313	9.593
Na_2CO_3	0.798	2.603	1.968	2.856	2.749	4.147
NH_3 water	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*

* Silica gel could not be obtained.

It was found that under all conditions, NaOH yielded the highest amount of silica gel, while Na_2CO_3 which is a general reagent for production of sodium silicate produced less than a half of silica gel from NaOH. On the other hand, NH_3 solution could not generate any silica gel. This may be explained by the basicity of each chemical (pK_b of NaOH = 0.2, pK_b of Na_2CO_3 = 3.60, pK_b of NH_3 = 4.75). NaOH is the strongest in basicity; therefore it can react with SiO_2 easily. $NaCO_3$ solution gave higher yield than NH_3 water because NH_3 gas evaporated from the solution at high temperatures. Using NaOH in MW heating has another advantage in that it does not make use of metal or glass reactors, which are sensitive to NaOH.

In this work, SiO_2/Na_2O ratio was also calculated for estimation of reaction efficiency. SiO_2/Na_2O ratio can be varied from 4 to 1, depending on the types of sodium silicates obtained. The example of SiO_2/Na_2O ratio for various types of sodium silicate is shown in Table 3.

Table 3. The composition of silicate products and their SiO_2/Na_2O ratio

Products	names	SiO_2/Na_2O ratio
$Na_2O{\cdot}SiO_2$	sodium metasilicate	1.0
$Na_2O{\cdot}4SiO_2$	sodium tetrasilicate	4.0
$2Na_2O{\cdot}SiO_2$	sodium orthosilicate	0.5
$Na_2O{\cdot}2SiO_2$	sodium disilicate	2.0

Generally, a high SiO_2/Na_2O value is preferable because the system needs lower equivalent of base (NaOH) for preparation and also a smaller amount of acid for neutralization for formation of silica gel.

Table 4 shows SiO_2/Na_2O ratio when the reactions were performed by using NaOH as the limiting reagent (< 0.33 mol) with moisture for 3 days. It was found that silica gel prepared by lower concentration of NaOH solution showed better adsorption ability than those gels

Table 4. Effect of concentration of sodium hydroxide solution on SiO_2 production and SiO_2/Na_2O ratio

Reaction conditions	400 W, 5 min						400 W, 10 min					
	50 ml			100 ml			50 ml			100 ml		
	0.5M	1.0M	2.0M	0.5M	1.0M	2.0M	0.5M	1.0M	2.0M	0.5M	1.0M	2.0M
SiO_2 (g)	1.37	1.51	1.71	1.54	3.51	4.61	1.84	2.95	-*	2.16	4.15	5.25
SiO_2/Na_2O	1.81	1.00	0.56	2.04	2.32	1.52	2.43	1.95	-*	2.85	2.74	1.73
Reaction conditions	800 W, 5 min						800 W, 10 min					
	100 ml			150 ml			100 ml			150 ml		
	0.5M	1.0M	2.0M	0.5M	1.0M	2.0M	0.5M	1.0M	2.0M	0.5M	1.0M	2.0M
SiO_2 (g)	2.21	2.47	4.74	2.99	3.80	5.84	-*	-*	-*	3.82	4.15	9.20
SiO_2/Na_2O	2.92	1.63	1.56	1.31	0.84	0.64	-*	-*	-*	1.68	0.91	1.01

Note: * No reaction was performed by this condition.

The results showed that reactions with high NaOH concentration usually resulted in low SiO_2/Na_2O (2.0 M NaOH were 0.64 -1.73) and that reactions with low NaOH concentration gave high SiO_2/Na_2O (0.5 M NaOH were 1.68 -2.92). SiO_2/Na_2O of 5 min reaction of 0.5 M NaOH by MW 800 W was as high as 2.92, which was higher than confirmed by any report for the reactions between quartz sand and NaOH solution.[7] The result implied that the silicate production from the reaction of rice husk ash and NaOH is worth further investigation for practical applications.

Effect of Condition of Extraction on Water Adsorption Ability of Silica Gel

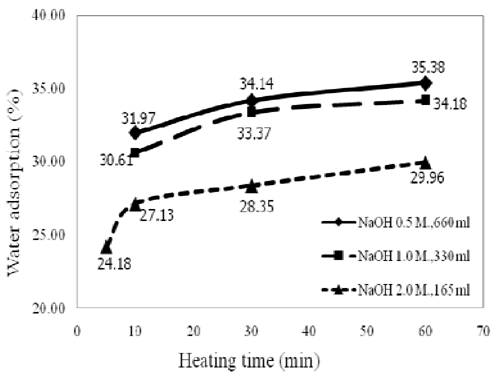

Figure 1. Effect of reaction conditions on water adsorpion (%) of silica gels from conventional heating.

Figure 1 shows water adsorption of silica gel from conventional heating. Each silica gel sample was placed in desiccator which was aturated prepared by high concentration of NaOH solution. Especially 0.5 M and 1.0 M of NaOH solution showed almost 20% higher adsorption ability than 2.0 M of NaOH solution. The silica gel that was prepared by longer reaction time had better adsorption ability than that of short-time reaction.

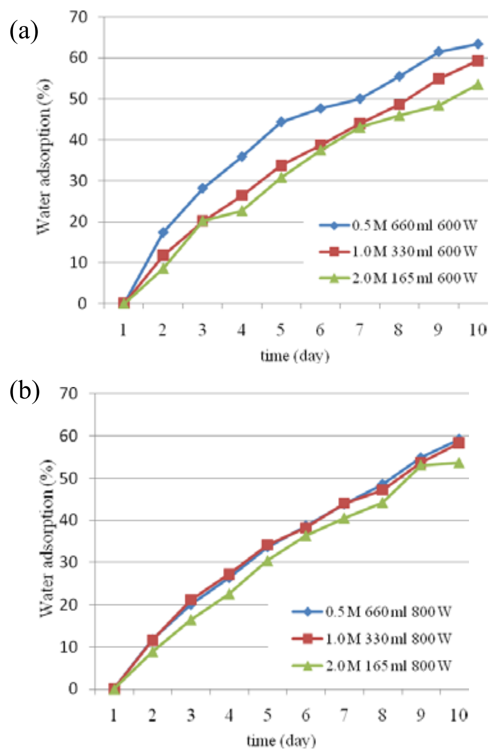

Figure 2. Effect of NaOH concentration on water adsorpion (%) of silica gels from microwave heating at 600 W (a) and 800 W (b).

Figure 2 shows the effect of NaOH concentration on water adsorpion (%) of silica gels. It was found that at 600 W, silica gel obtained from 0.5 M NaOH solution showed higher ability of water adsorption than silica gel prepared by 1.0 M and 2.0 NaOH solution. The different water adsorption abilities decreased when 800 W was used in preparation. The results implied that the using lower NaOH concentration and low MW power resulted in silica gel with high adsorption ability.

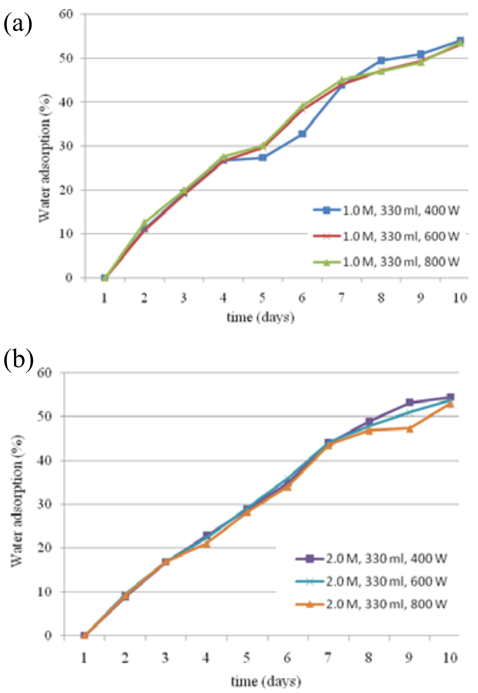

Figure 3. Effect of microwave power on water adsorpion (%) of silica gels at 1.0 M (a) and 2.0 M (b) of NaOH solution.

The results in Figure 3 were obtained by conductingthe reaction with different microwave power. It seemed that with the same concentration and volume of NaOH solution, there was no significant difference between use of high MW power and low MW power.

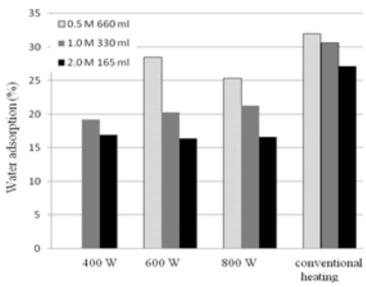

Figure 4. Comparison of water adsorption ability (3 days) between silica gel prepared by MW heating and conventinal heating.

Figure 4 shows water adsorption ability of silica gel prepared from different NaOH concentrations and MW power compared with that obtained from conventional heating. It can be seen that lower concentration of NaOH increased the adsorption ability of silica gel. However, silica gel from MW reaction (0.5 M, 600 W, 28.47%) that showed the highest adsorption ability was still lower than all kinds of silica gel from conventional heating (31.97%, 30.61%, 27.13%). Even though, the experiment of NaOH and rice husk ash which have NaOH as the limiting reagent, which has supposed to determine the SiO_2/Na_2O ratio was not performed in this report. The question whether the conventional heating produced a higher ratio of SiO_2/Na_2O than MW heating arises. The difference in adsorption ability between dielectric heating methods and conventional methods deserves further investigation.

Conclusions

Compared with conventional heating method in oil bath at 1500 W at the same reaction time, MW heating gave a higher yield of silica gel at 800 W by 0.5, 1.0 and 2.0 M NaOH solution. By reaction at 800 W with 1.0 M NaOH solution, the weight of silica gel obtained from MW (6.830 g) was almost 1.6 times that from conventional heating (3.997 g). And the reaction at 800 W with 2.0 M NaOH solution yielded 9.593 g of silica gel from 10 g of rice husk ash in 10 min. The results showed that MW heating is capable of extraction of silica gel from rice husk ash. Comparing concentrations of NaOH solution revealed that 0.5 M solution could give SiO_2/Na_2O ratio as high as 2.92 by heating at 800 W for 5 min.

Evaluation of water adsorption ability revealed that silica gel prepared by low concentration of NaOH solution had greater ability than that prepared by high concentration of NaOH solution. On the other hand, power of MW showed no effect on the adsorption ability. But all silica gels from MW reaction showed much less ability of water adsorption than those from conventional heating. Different types of sodium silicate were then considered to be formed from MW heating and conventional heating.

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